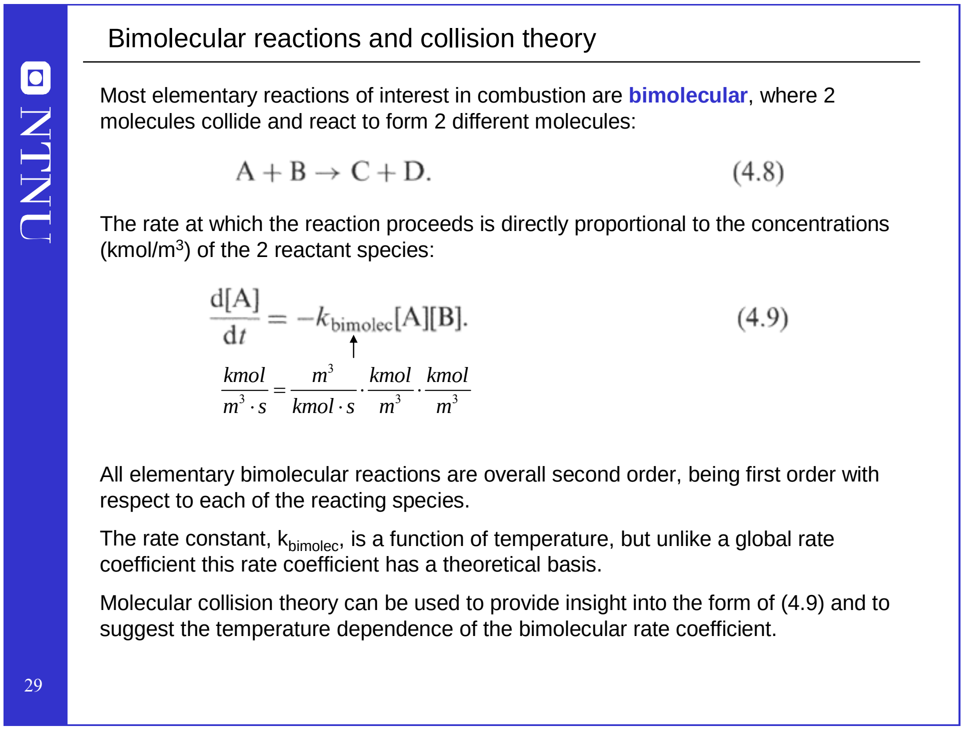
Oppgave 7

Sett opp prinsippielle reaksjonsligninger for unimolekylære, bimolekylære og termolekylære reaksjoner. Diskuter disse med hensyn til viktige karakteristika, f.eks. reaksjonsorden.

Løsningsforslag:



Bimolecular reactions and collision theory

Most elementary reactions of interest in combustion are **bimolecular**, where 2 molecules collide and react to form 2 different molecules:

$$A + B \rightarrow C + D. \qquad (4.8)$$

The rate at which the reaction proceeds is directly proportional to the concentrations (kmol/m^3) of the 2 reactant species:

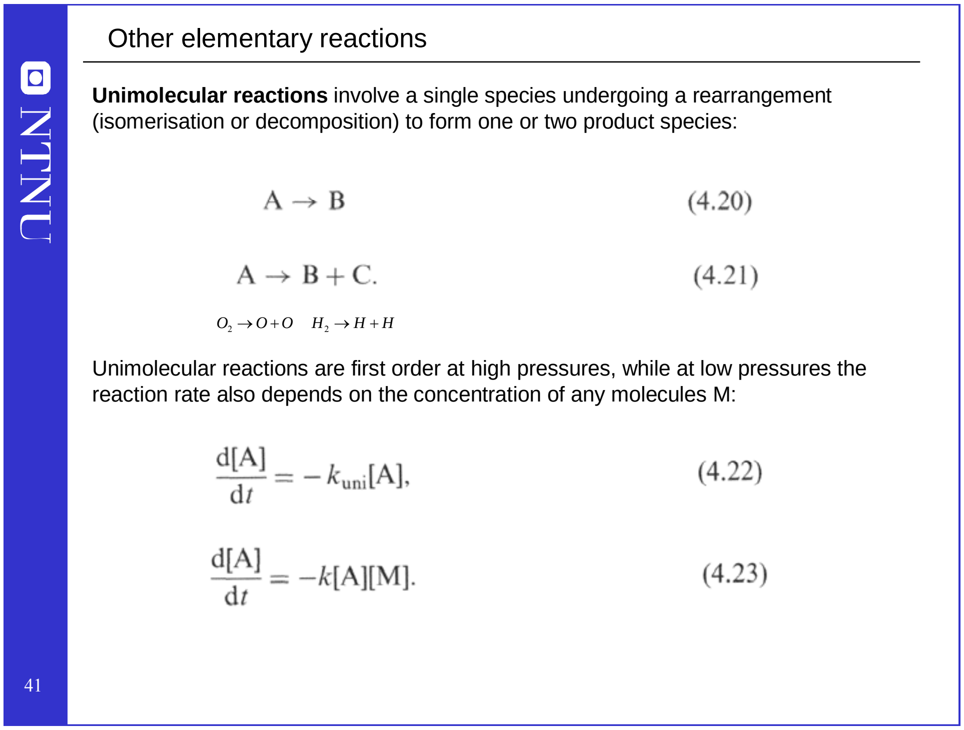
$$\frac{d[A]}{dt} = -\underset{\uparrow}{k_{\text{bimolec}}}[A][B]. \qquad (4.9)$$

$$\frac{kmol}{m^3 \cdot s} = \frac{m^3}{kmol \cdot s} \cdot \frac{kmol}{m^3} \cdot \frac{kmol}{m^3}$$

All elementary bimolecular reactions are overall second order, being first order with respect to each of the reacting species.

The rate constant, $k_{bimolec}$, is a function of temperature, but unlike a global rate coefficient this rate coefficient has a theoretical basis.

Molecular collision theory can be used to provide insight into the form of (4.9) and to suggest the temperature dependence of the bimolecular rate coefficient.



Other elementary reactions

Unimolecular reactions involve a single species undergoing a rearrangement (isomerisation or decomposition) to form one or two product species:

$$A \rightarrow B \qquad (4.20)$$

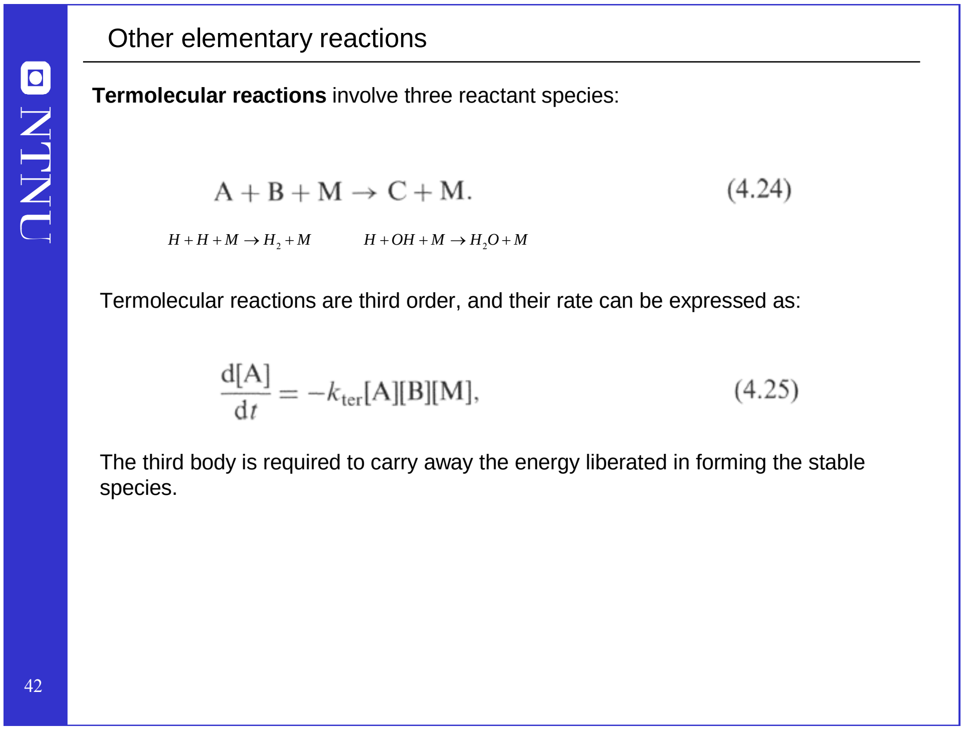
$$A \rightarrow B + C. \qquad (4.21)$$

$O_2 \rightarrow O + O \quad H_2 \rightarrow H + H$

Unimolecular reactions are first order at high pressures, while at low pressures the reaction rate also depends on the concentration of any molecules M:

$$\frac{d[A]}{dt} = -k_{uni}[A], \qquad (4.22)$$

$$\frac{d[A]}{dt} = -k[A][M]. \qquad (4.23)$$



Other elementary reactions

Termolecular reactions involve three reactant species:

$$A + B + M \rightarrow C + M. \qquad (4.24)$$

$H + H + M \rightarrow H_2 + M \qquad H + OH + M \rightarrow H_2O + M$

Termolecular reactions are third order, and their rate can be expressed as:

$$\frac{d[A]}{dt} = -k_{ter}[A][B][M], \qquad (4.25)$$

The third body is required to carry away the energy liberated in forming the stable species.

Oppgave 8

Zeldovich mekanismen for dannelse av NO fra N_2 er:

$$N_2 + O \underset{k_{1b}}{\overset{k_{1f}}{\rightleftarrows}} NO + N$$

$$N + O_2 \underset{k_{2b}}{\overset{k_{2f}}{\rightleftarrows}} NO + O$$

Konstruer, ved å gjøre visse begrunnede antagelser, en global reaksjonsligning $N_2 + O_2 \xleftrightarrow{k_G} 2NO$ med reaksjonsraten $\frac{d[NO]}{dt} = k_G[N_2]^m[O_2]^n$, dvs. finn et uttrykk for k_G, og finn m og n.

Løsningsforslag:

Because the second reaction is much faster than the first, the steady-state approximation can be used to evaluate the N-atom concentration. Furthermore, in high-temperature systems the NO formation reaction is typically much slower than other reactions involving O_2 and O. Thus O_2 and O can be assumed to be in equilibrium.

From the elementary reactions we can write

$$\frac{d[NO]}{dt} = k_{1f}[N_2][O] + k_{2f}[N][O_2]$$

$$\frac{d[N]}{dt} = k_{1f}[N_2][O] - k_{2f}[N][O_2]$$

where we assume that the reverse reaction rates are negligible.

Assuming steady-state for N (dN/dt=0) gives

$$[N]_{ss} = \frac{k_{1f}[N_2][O]}{k_{2f}[O_2]}$$

This gives

$$\frac{d[NO]}{dt} = k_{1f}[N_2][O] + k_{2f}\frac{k_{1f}[N_2][O]}{k_{2f}[O_2]}[O_2] = 2k_{1f}[N_2][O]$$

We eliminate [O] through our equilibrium assumption

$$K_p = \frac{\left(\frac{p_O}{p^0}\right)^2}{\frac{p_{O_2}}{p^0}} = \frac{p_O{}^2}{p_{O_2}p^0} = \frac{\left([O]R_uT\right)^2}{[O_2]R_uTp^0} = \frac{[O]^2R_uT}{[O_2]p^0}$$

or

$$[O] = \left([O_2]\frac{K_pp^0}{R_uT}\right)^{\frac{1}{2}}$$

Thus

$$\frac{d[NO]}{dt} = 2k_{1f}[N_2]\left([O_2]\frac{K_pp^0}{R_uT}\right)^{\frac{1}{2}} = 2k_{1f}\left(\frac{K_pp^0}{R_uT}\right)^{\frac{1}{2}}[N_2][O_2]^{\frac{1}{2}}$$

From the above we can identify the global parameters

$$\underline{\underline{k_G = 2k_{1f}\left(\frac{K_p p^0}{R_u T}\right)^{\frac{1}{2}}}}$$

$$\underline{\underline{m = 1}}$$

$$\underline{\underline{n = \frac{1}{2}}}$$

Oppgave 9

Diskuter CO mekanismen gitt nedenfor, og betydningen av de ulike reaksjonene under ulike reaksjonsbetingelser.

$$CO + O_2 \rightarrow CO_2 + O \quad (CO.1)$$

$$O + H_2O \rightarrow OH + OH \quad (CO.2)$$

$$CO + OH \rightarrow CO_2 + H \quad (CO.3)$$

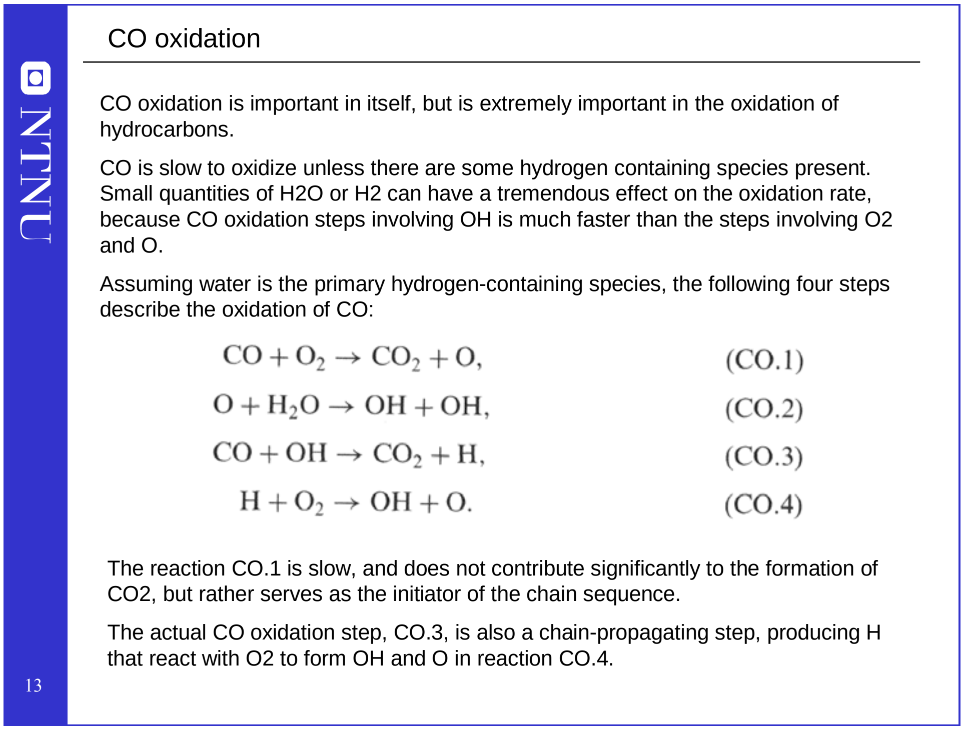
$$H + O_2 \rightarrow OH + O \quad (CO.4)$$

$$O + H_2 \rightarrow OH + H \quad (CO.5)$$

$$OH + H_2 \rightarrow H_2O + H \quad (CO.6)$$

$$CO + HO_2 \rightarrow CO_2 + OH \quad (CO.7)$$

Løsningsforslag:



CO oxidation

CO oxidation is important in itself, but is extremely important in the oxidation of hydrocarbons.

CO is slow to oxidize unless there are some hydrogen containing species present. Small quantities of H2O or H2 can have a tremendous effect on the oxidation rate, because CO oxidation steps involving OH is much faster than the steps involving O2 and O.

Assuming water is the primary hydrogen-containing species, the following four steps describe the oxidation of CO:

$$\mathrm{CO + O_2 \rightarrow CO_2 + O,} \qquad (\mathrm{CO.1})$$

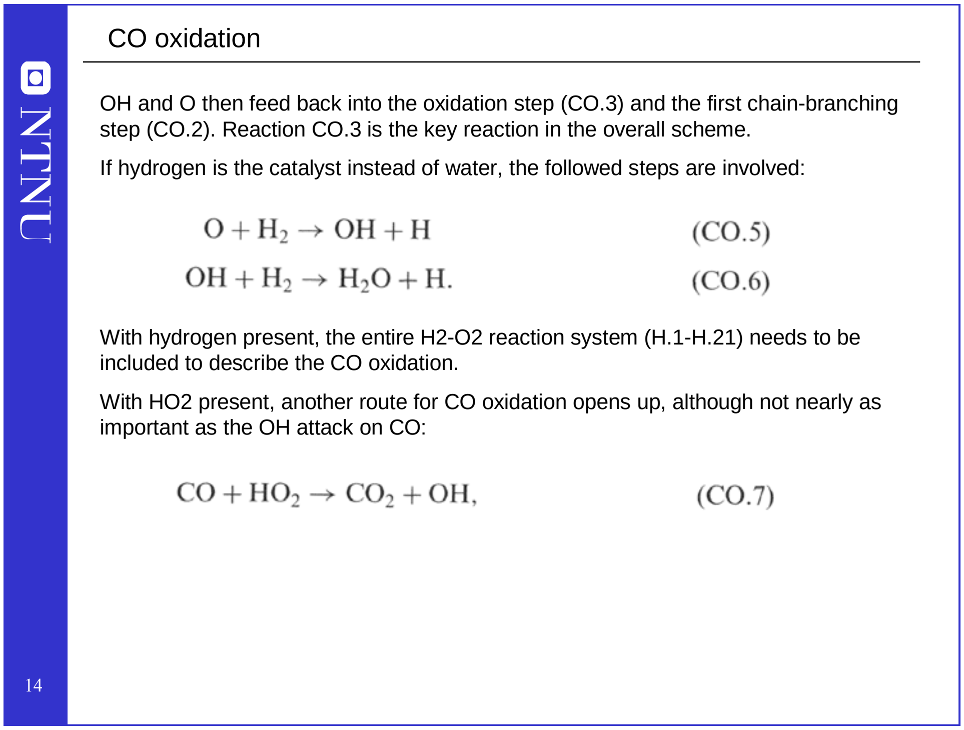
$$\mathrm{O + H_2O \rightarrow OH + OH,} \qquad (\mathrm{CO.2})$$

$$\mathrm{CO + OH \rightarrow CO_2 + H,} \qquad (\mathrm{CO.3})$$

$$\mathrm{H + O_2 \rightarrow OH + O.} \qquad (\mathrm{CO.4})$$

The reaction CO.1 is slow, and does not contribute significantly to the formation of CO2, but rather serves as the initiator of the chain sequence.

The actual CO oxidation step, CO.3, is also a chain-propagating step, producing H that react with O2 to form OH and O in reaction CO.4.



CO oxidation

OH and O then feed back into the oxidation step (CO.3) and the first chain-branching step (CO.2). Reaction CO.3 is the key reaction in the overall scheme.

If hydrogen is the catalyst instead of water, the followed steps are involved:

$$O + H_2 \rightarrow OH + H \qquad (CO.5)$$

$$OH + H_2 \rightarrow H_2O + H. \qquad (CO.6)$$

With hydrogen present, the entire H2-O2 reaction system (H.1-H.21) needs to be included to describe the CO oxidation.

With HO2 present, another route for CO oxidation opens up, although not nearly as important as the OH attack on CO:

$$CO + HO_2 \rightarrow CO_2 + OH, \qquad (CO.7)$$

Oppgave 10

a) Forklar en-film modellen, to-film modellen og kontinuerlig-film modellen for forbrenning av en karbonpartikkel. Tegn en figur som viser temperaturprofiler og konsentrasjonsprofiler i partikkelen og i atmosfæren rundt partikkelen i en en-film modell.

Løsningsforslag:

Burning of carbon

In the **one-film model** there is no flame in the gas phase and the maximum temperature occurs at the carbon surface. The one-film model is quite simple, useful for illustrating the combined effects of heterogeneous kinetics and gas-phase diffusion.

In the **two-film model**, a flame-sheet lies at some distance from the surface, where the CO produced at the surface reacts with incoming O2. The two-film model is still simplified, but shows more realistically than the one-film model the sequential production and oxidation of CO.

In the **continuous-film model**, a flame-zone is distributed within the boundary layer, rather than occurring in the flame-sheet.

Burning of carbon

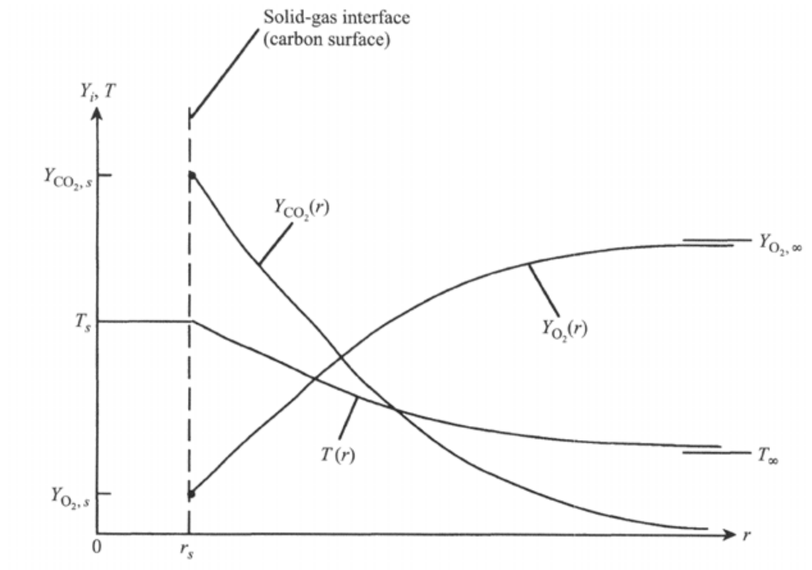


Figure 14.3 Species and temperature profiles for one-film model of carbon combustion assuming that CO_2 is the only product of combustion at the carbon surface.

Oppgave 11

Forbrenningsraten for karbonpartikkelen i en en-film modell kan utledes som

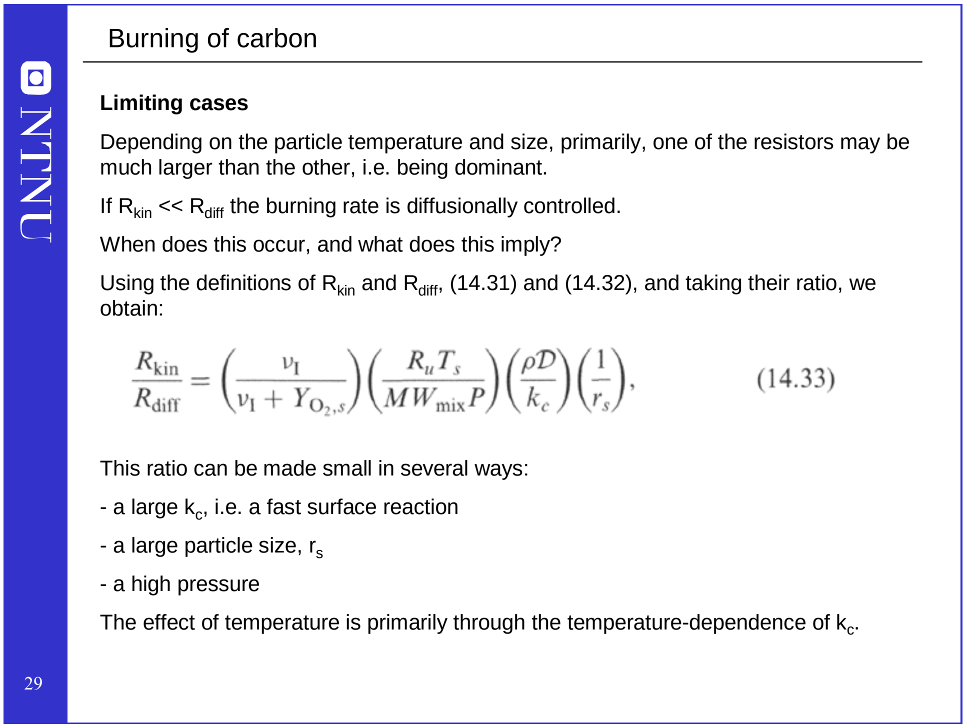
$$\dot{m}_C = \frac{Y_{O_2,\infty} - Y_{O_2,s}}{R_{kin} + R_{diff}}$$

$$R_{kin} \equiv \frac{\nu_I R_u T_s}{4\pi r_s^2 MW_{mix} k_c P}$$

$$R_{diff} \equiv \frac{\nu_I + Y_{O_2,s}}{\rho D 4\pi r_s}$$

Diskuter de ulike parameterenes innvirkning på forbrenningsraten. Når er forbrenningsraten diffusjonskontrollert og når er den kinetikkontrollert?

Løsningsforslag:



Burning of carbon

Limiting cases

Depending on the particle temperature and size, primarily, one of the resistors may be much larger than the other, i.e. being dominant.

If $R_{kin} << R_{diff}$ the burning rate is diffusionally controlled.

When does this occur, and what does this imply?

Using the definitions of R_{kin} and R_{diff}, (14.31) and (14.32), and taking their ratio, we obtain:

$$\frac{R_{\mathrm{kin}}}{R_{\mathrm{diff}}} = \left(\frac{\nu_{\mathrm{I}}}{\nu_{\mathrm{I}} + Y_{\mathrm{O}_2,s}}\right)\left(\frac{R_u T_s}{MW_{\mathrm{mix}} P}\right)\left(\frac{\rho \mathcal{D}}{k_c}\right)\left(\frac{1}{r_s}\right), \qquad (14.33)$$

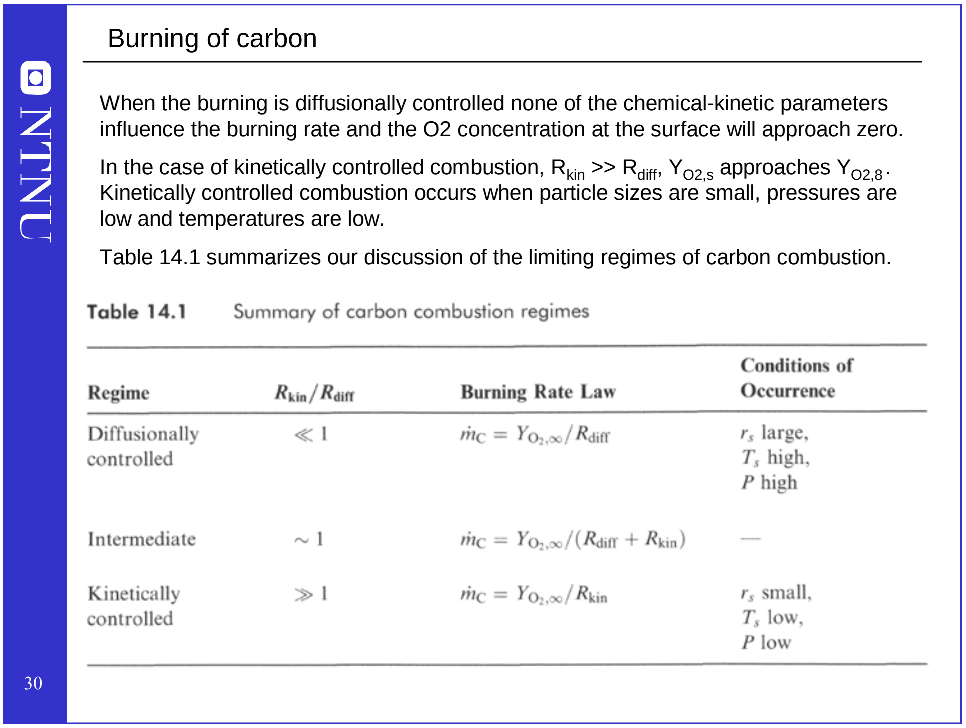
This ratio can be made small in several ways:

- a large k_c, i.e. a fast surface reaction

- a large particle size, r_s

- a high pressure

The effect of temperature is primarily through the temperature-dependence of k_c.



Burning of carbon

When the burning is diffusionally controlled none of the chemical-kinetic parameters influence the burning rate and the O2 concentration at the surface will approach zero.

In the case of kinetically controlled combustion, R_{kin} >> R_{diff}, $Y_{O2,s}$ approaches $Y_{O2,8}$. Kinetically controlled combustion occurs when particle sizes are small, pressures are low and temperatures are low.

Table 14.1 summarizes our discussion of the limiting regimes of carbon combustion.

Table 14.1 Summary of carbon combustion regimes

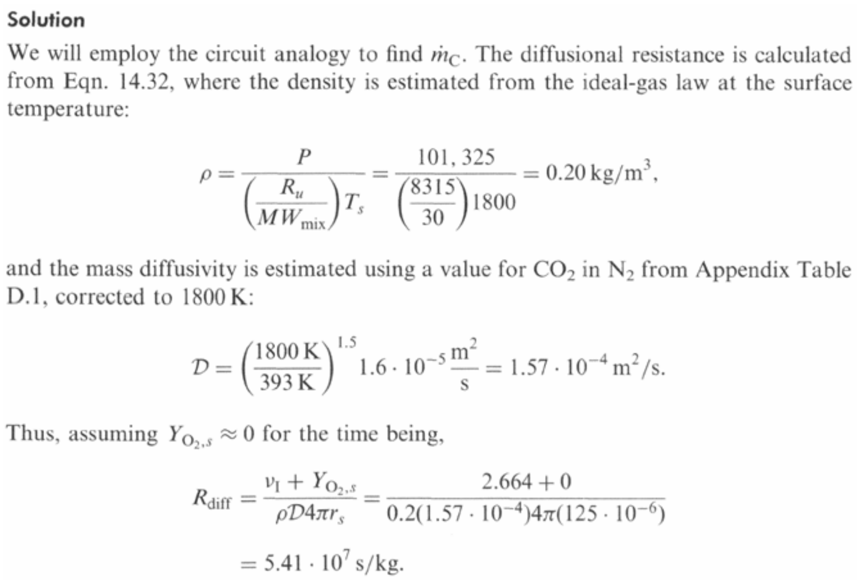
Regime	R_{kin}/R_{diff}	Burning Rate Law	Conditions of Occurrence
Diffusionally controlled	$\ll 1$	$\dot{m}_C = Y_{O_2,\infty}/R_{diff}$	r_s large, T_s high, P high
Intermediate	~ 1	$\dot{m}_C = Y_{O_2,\infty}/(R_{diff} + R_{kin})$	—
Kinetically controlled	$\gg 1$	$\dot{m}_C = Y_{O_2,\infty}/R_{kin}$	r_s small, T_s low, P low

Oppgave 12

Beregn forbrenningsraten til en 250 µm karbonpartikkel i stillestående luft (YO_2,∞ = 0,233) ved 1 atm ved å anta en en-film modell. Partikkeltemperaturen er 1800 K, og reaksjonskonstanten k_c er 13,9 m/s. Anta at midlere molekylvekt for gassene ved partikkeloverflaten er 30 kg/kmol. Er forbrenningsraten diffusjonskontrollert eller kinetikkontrollert?
Oppgitt: Diffusiviteten til CO_2 i N_2 ved 1800 K er 0,000157 m^2/s.

Løsningsforslag:

Burning of carbon – Example 14.1



Solution

We will employ the circuit analogy to find $\dot{m}_C$. The diffusional resistance is calculated from Eqn. 14.32, where the density is estimated from the ideal-gas law at the surface temperature:

$$\rho = \frac{P}{\left(\dfrac{R_u}{MW_{\text{mix}}}\right)T_s} = \frac{101,325}{\left(\dfrac{8315}{30}\right)1800} = 0.20\,\text{kg/m}^3,$$

and the mass diffusivity is estimated using a value for CO_2 in N_2 from Appendix Table D.1, corrected to 1800 K:

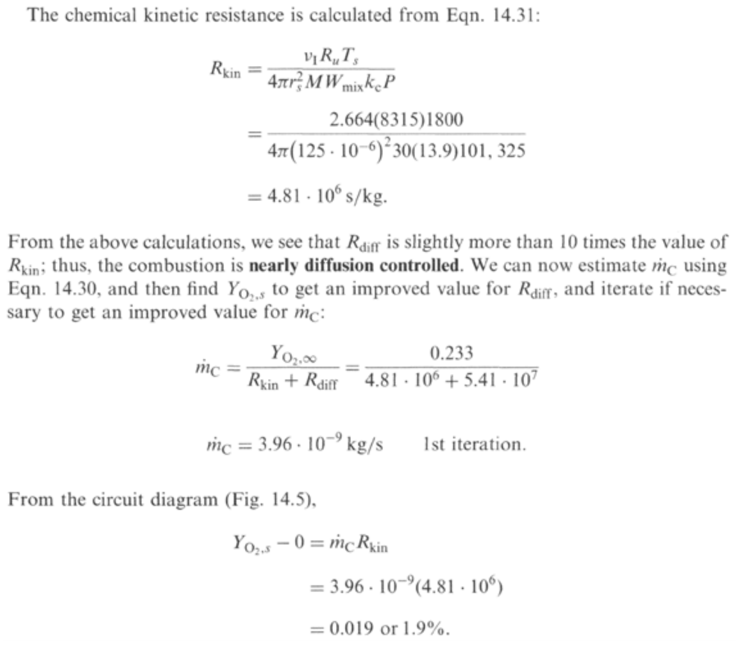
$$\mathcal{D} = \left(\frac{1800\,\text{K}}{393\,\text{K}}\right)^{1.5} 1.6 \cdot 10^{-5}\,\frac{\text{m}^2}{\text{s}} = 1.57 \cdot 10^{-4}\,\text{m}^2/\text{s}.$$

Thus, assuming $Y_{O_2,s} \approx 0$ for the time being,

$$R_{\text{diff}} = \frac{\nu_I + Y_{O_2,s}}{\rho \mathcal{D} 4\pi r_s} = \frac{2.664 + 0}{0.2(1.57 \cdot 10^{-4})4\pi(125 \cdot 10^{-6})}$$

$$= 5.41 \cdot 10^7\,\text{s/kg}.$$

Burning of carbon – Example 14.1



The chemical kinetic resistance is calculated from Eqn. 14.31:

$$R_{\text{kin}} = \frac{\nu_I R_u T_s}{4\pi r_s^2 MW_{\text{mix}} k_c P}$$

$$= \frac{2.664(8315)1800}{4\pi(125 \cdot 10^{-6})^2 30(13.9)101,325}$$

$$= 4.81 \cdot 10^6\,\text{s/kg}.$$

From the above calculations, we see that R_{diff} is slightly more than 10 times the value of R_{kin}; thus, the combustion is **nearly diffusion controlled**. We can now estimate $\dot{m}_C$ using Eqn. 14.30, and then find $Y_{O_2,s}$ to get an improved value for R_{diff}, and iterate if necessary to get an improved value for $\dot{m}_C$:

$$\dot{m}_C = \frac{Y_{O_2,\infty}}{R_{\text{kin}} + R_{\text{diff}}} = \frac{0.233}{4.81 \cdot 10^6 + 5.41 \cdot 10^7}$$

$$\dot{m}_C = 3.96 \cdot 10^{-9}\,\text{kg/s} \qquad \text{1st iteration.}$$

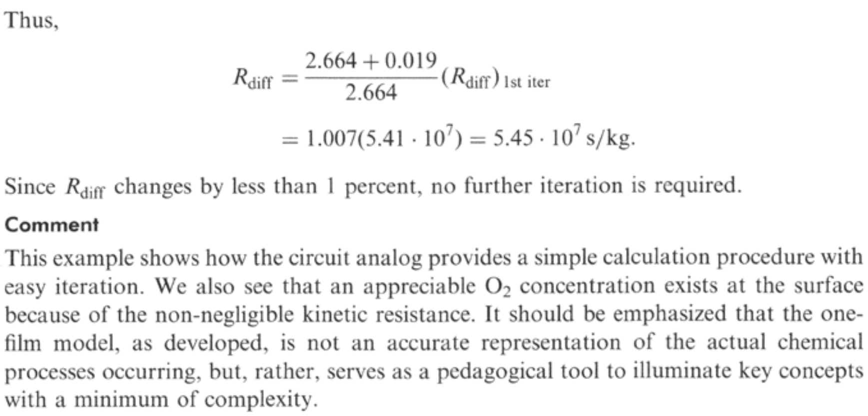
From the circuit diagram (Fig. 14.5),

$$Y_{O_2,s} - 0 = \dot{m}_C R_{\text{kin}}$$

$$= 3.96 \cdot 10^{-9}(4.81 \cdot 10^6)$$

$$= 0.019 \text{ or } 1.9\%.$$

Burning of carbon – Example 14.1



Thus,

$$R_{\text{diff}} = \frac{2.664 + 0.019}{2.664}(R_{\text{diff}})_{\text{1st iter}}$$

$$= 1.007(5.41 \cdot 10^7) = 5.45 \cdot 10^7 \text{ s/kg}.$$

Since R_{diff} changes by less than 1 percent, no further iteration is required.

Comment

This example shows how the circuit analog provides a simple calculation procedure with easy iteration. We also see that an appreciable O_2 concentration exists at the surface because of the non-negligible kinetic resistance. It should be emphasized that the one-film model, as developed, is not an accurate representation of the actual chemical processes occurring, but, rather, serves as a pedagogical tool to illuminate key concepts with a minimum of complexity.